5/19/88

Shaughnessy No: 034401

Date Out of EAB: MAY 19 1988

TO: William Miller/Daniel Peacock
Product Manager #16
Registration Division (TS-767C)

FROM: Emil Regelman
Environmental Chemistry Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

THRU: Paul F. Schuda, Chief
Exposure Assessment Branch/HED (TS-769C)

Attached, please find the EAB review of:

Reg./File #: 239-1633; 239-1721

Chemical Name: NALED

Type product: Insecticide/Acaricide

Product Name: DIBROM

Company Name: Chevron Chemical Company

Purpose: Review of studies (concern for contribution of naled to DDVP formation); Request by company to use data from Aquatic Field Dissipation to fulfill data for Accumulation- Irrigated Crops

Date Received: a) 1/26/88; b) 2/18/88 c) 3/17/88; d) 4/14/88

Action Code: 660

Date Completed: 5/19/88

EAB #(s): a)80337; b)80432-34 c)80530; d)80656-58

Monitoring study requested: _____

Total Reviewing Time: 6 days

Monitoring study volunteered: _____

Deferrals to: _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1. Chemical: Common name:

Naled

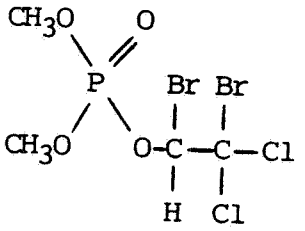
Chemical name:

1,2-Dibromo-2,2-dichloroethyl dimethyl phosphate

Trade name(s):

RE 4355, Bromex, Dibrom

Structure:



Structures of the degradates of naled are shown at the end of the review.

Formulations:

3-6% D, 7-15% Impr, 2-7.2 lb/gal and 2.5-58% EC, 12.6 lb/gal and 1.2-20% SC/L, 1.26-3.34 lb/gal and 0.66-15% RTU.

Physical/Chemical properties:

Molecular formula: $C_4H_7O_2PCl_2Br_2$
Molecular weight: 348.6
Physical state: Yellow liquid, slightly pungent odor
Melting point: 26.5-27.5° C
Vapor pressure of ai: 2 X $10^{-4}$mm Hg at 20° C
Solubility: Practically insoluble in water. Freely soluble in aromatic and chlorinated hydrocarbons, ketones, and alcohols. Sparingly soluble in petroleum solvents and mineral oils.

2. Study/Action Type: Addendum to the Naled Registration Standard.

3. Study ID: Selman, F. and Williams, M. (1987) Dissipation study on DIBROM 14 concentrate for forestry uses. ABC Report No. 33770. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO; and submitted by Chevron Chemical Co., Richmond, CA. (40304301).

Chen, Y.S. 1986a. Hydrolysis products of (ethyl-1-$^{14}$C)naled in buffer solutions. Laboratory Project Identification 8602408. Unpublished study prepared and submitted by Chevron Chemical Company, Richmond, CA. (40034902)

Chen Y.S. 1986b. Photodegradation of ethyl-1-[$^{14}$C]naled in water by long wavelength UV light. Laboratory Project Identification 8613174. Prepared and submitted by Chevron Chemical Company, Richmond, CA (40034903)

Chen, Y.S. 1987. Naled photolysis on dead cotton leaves. Laboratory Project Identification MEF-0049/8720594. Prepared and submitted by Chevron Chemical Company, Richmond, CA (403573-00)

Cheng, H.M. 1986. Naled accumulation study: Rotational crops (confined). Laboratory Project ID: 8607629A. Prepared and submitted by Chevron Chemical Company, Richmond, CA. (40034905)

Lee, S.L. 1988. Aquatic field dissipation of DIBROM. Laboratory Project ID: R196T71178. Prepared and submitted by Chevron Chemical Company, Richmond, CA (40494100)

Pack, D.E. 1986a. The aerobic aquatic metabolism of (ethyl-1-$^{14}$C)naled (DIBROM). Laboratory Project Identification 8607764. Prepared and submitted by Chevron Chemical Company, Richmond, CA Reg. No. 263621. (263621)

Pack, D.E. 1986b. Soil column leaching of (ethyl-1-$^{14}$C) naled (DIBROM). Laboratory Project Identification 86077623. Prepared and submitted by Chevron Chemical Company, Richmond, CA (263622)

Pack, D.E. 1987. Estimation of soil adsorption coefficient of naled from TLC data. Laboratory Project Identification MEF-0051/8711318. Unpublished study prepared and submitted by Chevron Chemical Company, Richmond, CA (402792-00)

Pack, D.E. 1986. Freundlich adsorption isotherms of dichloroacetic acid. Laboratoyr Project ID: 8614820. Prepared and submitted by Chevron Chemical Company, Richmond, CA (400349-04)

Pack, D.E. and Fry, C.E. 1988. Anaerobic aquatic metabolism of [ethyl-1-$^{14}$C] naled. Laboratory Project ID: MEF-0012/8716931. Prepared and submitted by Chevron Chemical Company, Richmond, CA (40580000)

Teeter, D. 1986. Determination of vapor phase photolysis rate of naled. Laboratory Project ID: ABC 34595. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Chevron Chemical Company, Richmond, CA (40050901)

4. Reviewed By: S.C. Termes
Chemist
EAB/HED/OPP

Signature:

Date: May 19th, 1988

5. Approved By: E. Regelman
Supervisory Chemist
Review Section #3
EAB/HED/OPP

Signature:

Date: MAY 19 1988

6. Conclusions:

I. The following studies were considered unacceptable:

° Hydrolysis -

Thin layer chromatography (TLC) on silica gel plates was the only methodology used to identify degradates (in the photodegradation in air study it is mentioned that naled is unstable on silica gel). Two apparently different unknowns were detected. Although the degradates were present at less than 10 percent, attempts should have been made to identify these unknowns since the Agency is concerned about the

contribution of naled to the concentration of DDVP in the environment (that is, DDVP is a degradate of concern).

The reported results indicate that the hydrolysis of naled is pH-dependent, with the rate of hydrolysis increasing with increasing pH. Different mechanisms predominate at pH 5 and at pH 9. At pH 9, the predominant mechanism is demethylation of naled to yield desmethyl naled as main degradate. At pH 5, cleavage of the P-O bond and elimination of the C(2)-Br predominates to yield bromodichloroacetaldehyde (BDCA) as main degradate. At neutral pH, both mechanisms appear to take place. Reported half-lives were 1.6 hours (pH 9); 15.4 hours at pH 7, and 96 hours (pH 5).

- Photodegradation in water -

The experiment was performed in a narrow-wavelength region (320-380 nm). No electronic absorption spectrum of naled under the experimental conditions (solvent, buffer system, etc.) was provided. Naled was introduced as an acetone solution. Acetone is a well-known photosensitizer; however, no comments were made in the study about any possible effects of acetone on the photodegradation of naled. Thin layer chromatography was the only methodology used to identify degradates.

The reported results indicate that naled degraded in a pH 5 buffer solution with a half-life of approximately 30 hours. Major degradates detected were bromodichloroacetaldehyde (BDCA, maximum 38.5% at 72 hours), DDVP (11.9% at 48 hours), acetic acid (15.7% at 96 hours); chloroacetic acid (CAA) plus dichloroacetic acid (DCAA) totaled a maximum of 13.4% at 96 hours. The only volatile product was $^{14}CO_2$ (8.2% after 96 hours).

- Photodegradation on leaves: (performed in place of photodegradation on soil)

The experiments (conducted under sunlight) were carried out in two days in which the atmospheric conditions were rather different, which provided unidentical incubation conditions for the samples. Thus, an accurate calculation of the rate of photodegradation was not possible under the experimental conditions.

From the reported results, DDVP reached a maximum concentration of 37.4 % of the applied at 2 hours posttreatment and 4.9 % after 4 hours. However, samples at 2 hours posttreatment and 4 hours post-treatment were taken on two separate, meteorologically dissimilar days (sunny with patches of clouds for the 2-hour samples; cloudy with spotty sunshine for the 4-hour samples). Therefore, it cannot be determined if continued exposure to sunlight would result in higher concentrations of DDVP on leaf surfaces.

- Photodegradation in air -

  Air samples were never analyzed separately from nonvaporized naled and, thus, degradation in the vapor phase could not be distinguished from degradation that occurred in material adsorbed to the sides of the glass container. Up to 81% of the applied radioactivity was not identified. The artificial light source was not similar to that of natural sunlight.

- Aerobic aquatic metabolism -

  The material balances were incomplete. Residues were incompletely characterized (extracts containing 0.23 ppm naled were not analyzed for degradates and degradates present up to 0.318 ppm were not identified). The test water was not characterized.

- Anaerobic aquatic metabolism -

  Relavant data was missing from the submitted report and, therefore, this study could not be evaluated at the present time.

- Mobility - soil column leaching -

  This study may be reevaluated if the registrant addresses the deficiencies noted in the RECOMMENDATIONS section.

  The reported results indicated that residues of aged (0.4-3 hours) naled were very mobile in sand soil columns, with 2.71 % of the applied radioactivity remaining in the soil (in general, evenly distributed throughout the columns) and 66.68 % in the leachates. Less than 0.002 ppm was parent naled; DDVP, dichloroethanol (DCE), and dichloroacetic acid (DCAA) were less than 0.093, 0.085, and 1.863 ppm, respectively. A species attributed to inorganic carbonate was present at less than 0.282 ppm.

- Mobility - estimation of adsorption coefficient of naled from (soil) TLC data -

  $K_d$ values were calculated from $R_f$ values reported in a previously submitted study (MRID 0064796). However, the mobility classification for naled differs in both studies. In the previous study, naled was classified as slightly mobile while with the mobility based on calculated $K_d$ values, naled would be classified as very mobile. Although the mobility of DDVP was reported in the old study, no $K_d$ values were calculated for this degradate in the new study.

- Mobility - Freundlich adsorption isotherms of dichloroacetic acid -

  Dichloroacetic acid (DCAA) was a major degradate found in leachates (soil column study). The submitted study is unacceptable because it was not established that the "equilibration time" of one hour was sufficient for the soil-solution slurries to reach equilibrium (this should have been established in a preliminary experiment). Also, the desorption phase of the study was not carried out.

- Aquatic field dissipation -

  Additional information (see RECOMMENDATIONS section) must be submitted by the registrant for reevaluation of this study. The typographical error on page 51, for which the registrant submitted a correction at a later day, was taken into account.

- Field dissipation - forestry -

  Insufficient data were provided to accurately establish a pattern of degradation of naled and its degradate DDVP in a forest environment. No frozen storage stability data were provided to confirm that samples did not degrade prior to analysis.

- Accumulation - rotational crop -

  The rotational crop (confined) study is not acceptable because: a) residues in the soil were not characterized, except at time 0; b) at time 0, the measured concentration of naled residues in the 0- to 6-inch soil depth was 0.52 ppm instead of the approximately 1 ppm expected for the 2 lb ai/A application; c) soil textured analysis could not be confirmed; d) immature plant samples were not analyzed. This study (40034905)

had the purpose of providing residue information on the amount and nature of residues taken up by rotational crops, which was requested in a review dated 8/5/86.

II. The registrant's request that the Aquatic Field Dissipation Study (164-1) be accepted to fulfill requirements for data on Accumulation-Irrigated Crops (165-3) cannot be considered until data requirements for the Aquatic Field Dissipation Study have been fulfilled.

III. Formation of DDVP From Naled Based on Data Reported by the Registrant (Unacceptable Studies; SEE DISCUSSION OF INDIVIDUAL STUDIES)

DDVP formation was observed in the photodegradation of naled at pH 5 (maximum 11.9% at 48 hours), in the photodegradation on surfaces of leaves (maximum 37.8% of the applied at 2 hours posttreatment under mostly sunny conditions and in "minor" amounts in the photodegradation in air.

DDVP was also observed in the aerobic aquatic metabolism studies, reaching a maximum concentration of less than 0.209 ppm at 1-day posttreatment but not being detected after 30 days posttreatment. (The anaerobic aquatic metabolism study was not reviewed because of missing data).

DDVP was present in the leachates of aged residues of naled in soil columns. Early studies (soil TLC) had indicated that DDVP was moderate mobile but in a submitted recalculation of mobility of naled DDVP was not included. According to the registrant, no dissipation rates (aquatic field dissipation studies) could be established for naled/DDVP because the residues in pond water were too low and because no residues were found in sediment samples. In forestry dissipation studies, data was insufficient to establish the pattern of dissipation of naled and DDVP.

In accumulation in crops (confined) studies, no apparent attempts were made to identify any DDVP residues.

7. Recommendations:

161-1 - Hydrolysis

1. Actual representative, TLC data for hydrolysis experiments must be provided.



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2. The registrant must present convincing evidence that "unknown I" and "unknown II" were not DDVP.

3. New studies may be required if the identities of "unknown I" and "unknown II" cannot be clearly established. If new studies are to be performed, the identity of degradates should be confirmed by another methodology besides TLC.

4. Drastic changes in pH in sampling procedures should be avoided (please refer to Recommendation No.5 for soil column leaching studies).

161-2 - Photodegradation in Water

A new study is required, for which the following is required/recommended:

1. That the studies be conducted under natural sunlight.

2. The electronic absorption spectrum of naled and expected degradation products (including molar absorptivities) under the same experimental conditions (buffer system, etc.) must be reported.

3. The use of acetone to introduce naled in solution should be avoided since acetone is a well-known photosensitizer.

4. Identification/confirmation of photoproducts be done by other methodology besides TLC.

5. Control experiments be fully described and pertinent data presented.

6. See also Recommendation No.5 for soil column leaching studies.

161-3 - Photodegradation on Leaves (in Place of Photodegradation on Soil)

A new study is required for which the following is recommended:

1. Enough samples be taken in days of similar meteorological conditions are to be able to establish the effect of atmospheric conditions on the degradation pattern of naled.

2. The registrant clearly defines the exact position of the labeled carbon.

161-4 - Photodegradation in Air

New studies are required for which the following is recommended:

1. An improved experimental design that would allow sampling of gaseous phase independent of the liquid phase.

2. Use of adequate analytical methodology to identify photoproducts. The TLC method used in the submitted study appeared to be inadequate.

3. That the studies be conducted under natural sunlight conditions.

4. Submission of a protocol prior starting these studies is strongly suggested.

162-3 - Anaerobic Aquatic Metabolism

The study will be reevaluated upon submission by the registrant of the following information:

1. Table I (soil characteristics) and Table II (Phase I - Quantitation of Volatile Metabolites).

2. Analytical data for the bog water.

3. Flow rate of nitrogen and measurements of dissolved oxygen levels to insure that anaerobic conditions were maintained at all times throughout the duration of the experiments.

162-4 - Aerobic Aquatic Metabolism

A new study is required. Particular attention must be given to:

1. Material balances.

2. Identification/characterization of degradates at concentrations greater than 0.01 ppm. Additional methodology other than TLC must be used to confirm identify of degradates.

3. Analysis of test (bog) water must be included in the report.

4. The registrant should not assume (as it was the case with the reviewed study) that all distillates from different samples contain the same degradates(s). Distillates should be individually analyzed.

5. The rate at which air was bubbled through must be specified. Dissolved oxygen (DO) content and pH should be monitored throughout the duration of the experiment.

163.1 - Column Leaching

The study may be acceptable if the registrant satisfactorily addresses the following points:

1. Why $^{14}CO_2$ evolution was not monitored?

2. Clarify if solution drained overnight from the columns was collected and analyzed.

3. Correct discrepancies in Tables 12 and 16 and in Tables 5 and 6.

4. Correct textural classification for soil coded 6073-39.

5. Since a metabolite not previously observed by HPLC was attributed to inorganic $^{14}C$-carbonate, the registrant should consider the pH-dependent/$HCO_3^-/CO_3^{2-}$ distribution in leachates. In the hydrolysis and photodegradation studies in water it was noted that samples were acidified with

concentrated, strong mineral acids prior analysis or extraction. The rapid acidification could have destroyed any carbonate, if present. To confirm the presence of carbonate the registrant may consider the possibility of using ion chromatography.

163-1 - Mobility Studies (Calculation of $K_d$ Values From Soil Thin Layer Chromatography)

The registrant must be able to explain why the discrepancy in classifying the mobility of naled from $R_f$ values and from $K_d$ values. $K_d$ values for DDVP should also be calculated.

163-1 - Mobility Studies (Freundhich Adsorption Isotherms of the Degradate Dichloroacetic Acid)

A new study is required for which:

1. The equilibration time is established in a preliminary experiment.

2. The desorption phase of the study is also conducted and the results reported.

164-2 - Aquatic Field Dissipation

The following information must be submitted for reevaluation of the study:

1. Provide data on soil/sediment characteristics which were not included in the report.

2. Provide analytical data for pond water.

3. Clarify why, although in the description of the sampling procedures it was said that "upon retrieval of the core, the samples were separated into 0 to 7.5 cm and 7.5 to 15 cm sections" (then the respective sections at each sampling site were combined), no data for each of these separate sections appeared in the report. Therefore, pertinent data must be provided.

4. Dichloroacetic acid (DCAA) and dichloroethanol (DCE) were identified as degradation products in both aerobic/anaerobic aquatic metabolism studies; an explanation as to

why no apparent attempts were made to identify these metabolites in the aquatic field dissipation study must be given.

5. Provide a more complete, satisfactory description of the test sites.

164-3 - Forestry Dissipation

New studies may be required since the pattern of degradation of naled and DDVP could not be accurately determined.

1. Analytical method must be satisfactorily improved to allow analysis of samples.

2. Storage stability data must be established for the type of samples analyzed.

3. Data from all soil depths collected must be reported.

165-1 - Rotational Crops (Confined)

The registrant, must provide explanation as to why:

1. Residues were only characterized at time 0.

2. The measured concentration in the 0- to 6-inch soil depth was 0.52 ppm instead of the approximately 1 ppm expected for an application rate of 2 lb ai/A.

3. Immature plant samples were not analyzed.

4. The soil data (mechanical analysis) must be checked as to why sand, silt, and clay content adds up to 92% instead of 100%.

The registrant's request that the Aquatic Field Dissipation Study (164-1) be accepted to fulfill requirements for data on Accumulation - Irrigated Crops (165-3) cannot be considered until data requirements for the Aquatic Field Dissipation have been fulfilled.

A summary of data requirements for naled and their status is presented in Table I.

TABLE I

Naled is registered for the following uses: Terrestrial food crop (field, vegetable, and orchard crops); Terrestrial nonfood (livestock and poultry and their surroundings); Greenhouse food crop; Greenhouse nonfood; Domestic outdoor (urban and rural outdoor areas for mosquito control), Aquatic food crop; Aquatic nonfood; Forestry; Indoor uses (agricultural, domestic, medical and commercial establishments)

The following TABLE summarizes the environmental fate data requirements for all of these uses and the current status of the data.

| Data Requirements | Status | Review Date |
|---|---|---|
| 161-1 Hydrolysis | Not fulfilled | This review |
| 161-2 Photodegradation in water | Not fulfilled | This review |
| 161-3 Photodegradation on leaves (in place of photodegradation on soil) | Not fulfilled | This review |
| 161-4 Photodegradation in air | Not fulfilled | This review |
| 162-1 Aerobic soil metabolism | Fulfilled | 8/5/86 |
| 162-2 Anaerobic soil metabolism (Anaerobic aquatic metabolism study would fulfill this requirement) | Not fulfilled | This review |
| 163-1 Mobility: | | |
| Column leaching (aged soil) | Not fulfilled | This review |
| Soil TLC | Not fulfilled | This review |
| Adsorption of dichloroacetic acid (mobile degradate) | Not fulfilled | This review |
| 163-2 Volatility (Laboratory) | Not fulfilled | 9/17/87 |
| 163-3 Volatility (Field) | Reserved depending on results of laboratory studies | |
| 164-1 Field (soil) dissipation | Waiver granted | 8/5/86 |
| 164-2 Field (aquatic sediment) dissipation | Not fulfilled | This review |
| 164-3 Field (forestry) dissipation | Not fulfilled | This review |
| 165-1 Rotational crops (confined) (Accumulation) | Not fulfilled | 8/5/86 and this review |
| 165-2 Rotational crops (field) (Accumulation) | Reserved depending on results of confined studies (8/5/86) | |
| 165-3 Accumulation - Irrigated crops* | Not fulfilled | This review |
| 165-4 Accumulation- Fish | Satisfied | 8/5/86 |
| 165-5 Accumulation- Aquatic non-target | Satisfied | 8/5/86 |

*CHEVRON CHEMICAL COMPANY has requested (3/31/88) that the submitted Aquatic Field Dissipation Study (161-1) be accepted to fulfill requirements for data on Accumulation- Irrigated Crops (165-3). The former study was not acceptable and cannot fulfill data requirements for Accumulation-Irrigated Crops at the present time.

8. Background:

Introduction

The Agency is concerned about the hazards of naled products breaking down to DDVP and the contribution that naled application may make to the exposure of people. DDVP is currently under Special Review. Other related actions: DYLOX (trichlorfon).

Directions for Use

Naled is a nonsystemic insecticide-acaricide registered for use on terrestrial food crop (field, vegetable, and orchard crops), terrestrial nonfood (live-stock and poultry and their surroundings), greenhouse food crop, greenhouse nonfood, domestic outdoor (urban and rural outdoor areas for mosquito control), aquatic food crop, aquatic nonfood, forestry, and indoor (agricultural, domestic, medical, and commercial establishments) use sites. Of the naled applied in the United States, the major use sites are: fruit, nut, vegetable, and field crops (50%); mosquito control (35%); dog flea collars (10%); and livestock (5%). Single active ingredient formulations consist of 3 to 6%, D, 7 to 15% Impr, 2 to 7.2 lb/gal and 2.5 to 58% EC, 12.6 lb/gal and 1.2 to 20% SC/L, and 1.26 to 3.34 lb/gal and 0.66 to 15% RTU. Application rates range from 0.01 to 4 lb/A, 4.5 to 6.75 oz/50,000 $ft^3$ (7.2 lb/gal EC) and 16.67 to 50 fl oz/50,000 $ft^3$ (10% RTU) (greenhouse fumigation), 20 fl oz/5000 $ft^2$ (1% RTU), and 800 ppm (sewage). Naled is applied using aircraft and ground equipment including mist sprayers and foggers. Applicators need not be certified to apply naled.

9. Discussion of Individual Tests or Studies:

See attached reviews of individual studies.

10. Completion of One-Liner: No one-liner completed.

11. CBI Appendix:

All data reviewed here are considered "company confidential" by registrant and must be treated as such.